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(54) Extraction of vitamin E, phytosterols and squalene from palm oil

Extraktion von Vitamin E, Phytosterolen und Squalen aus Palmöl

Procédé d'extraction de vitamine E, phytosteroles et squalène à partir d'huile de palme

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- **CHOO Y-M ET AL: "RECOVERED OIL FROM PALM-PRESSED FIBER: A GOOD SOURCE OF NATURAL CAROTENOIDS, VITAMIN E, AND STEROLS" JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, AMERICAN OIL CHEMISTS' SOCIETY. CHAMPAIGN, US, vol. 73, no. 5, 1 May 1996 (1996-05-01), pages 599-602, XP000647324 ISSN: 0003-021X**

EP 1 394 144 B1

Description

FIELD OF INVENTION

[0001] The invention relates to the extraction of phytosterols, squalene and vitamin E from crude palm oil. More particularly the present invention relates to an integrated process to extract phytosterols, squalene and vitamin E from crude palm oil.

BACKGROUND OF THE INVENTION

[0002] Palm oil contains 700-1000 ppm of vitamin E, 300-620ppm of phytosterols and 250-730ppm of squalene. The present invention relates to a process for the recovery of the natural occurring Vitamin E, phytosterols and squalene from crude palm oil.

[0003] Vitamin E is a group of natural occurring lipid soluble antioxidants, namely tocopherols and tocotrienols that are found in certain vegetable oils. The main occurrence of tocotrienols is in palm oil, wheat germ oil, coconut oil and corn oil. Tocotrienols possess higher antioxidant activity than tocopherols, which have been shown in biochemical studies (Serbinova et al., 1991, Pokorny, J 1987 and Jacobsberg et al 1978). As a predominant type of vitamin E constituting 80% of total vitamin E found in palm oil, tocotrienols have also been known to possess hypocholesterolenic effect (Tan et al 1991 and Qureshi et al 1991).

[0004] Phytosterols are structurally similar to cholesterol except they are alkylated at the 24 position in the side chain. The most abundant type of phytosterols by far found in plants are β-sitosterol, stigmasterol and campesterol. These compounds are natural components of diet and are consumed in amounts of 100-500 mg/day with respect to US consumption (Weirauch, JL Gradner, JM 1978. Sterol content of foods of plant origin. J Am, Diet Assoc. 73:39-47). Studies conducted employing β-sitosterol were found to significantly reduce the amount of cholesterol in the blood (Farguhar, J W et al 1956. Circulation, 14,77-82). Palm oil is rich in phytosterols with 60% of β-sitosterol and the remaining 38% is stigmasterol and campesterol. Therefore it provides a natural source of phytosterols for recovery,

[0005] Squalene is a major component in various deep-sea shark liver oils. It is a powerful antioxidant that can scavenge free radicals from the body before they start their debilitating effect. Trials have shown that where squalene is taken as a dietary supplement, evidence has shown that it has preventative effects against carcinogenesis.

[0006] Squalene presents as one of the minor components in palm oil. It could be recovered as a valuable antioxidant if presented in high concentration.

[0007] EP 1 097 985 A describes methods for chromatographic isolation of non-glyceride components including Vitamin E, sterols and squalene from oils and fats using supercritical fluid in combination with adsorbents such as silica gel.

[0008] WO01/32682 describes methods for purification of phytosterols from vegetable fats and oils.

[0009] EP 992 499 A describes isolation of tocopherols and sterols from oils and fats by methods which comprise esterification of the fatty acids with an alcohol, transesterification with a basic catalyst and distillation to remove the fatty acid methyl esters.

[0010] WO0009535, GB 531226, GB 549931, GB 531224 and EP 0541999 concentrate on the recovery of vitamin E or vitamin E and phytosterols but not as an integrated process for the recovery of vitamin E, phytosterols and squalene together as described in this invention. These methods only proceed with one stage vacuum distillation in which it does not serve for the removal of high molecular weight components as described In this invention. Therefore, it is an objective of this invention to provide a method for purifying and recovering of these valuable minor compounds namely vitamin E, phytosterols and squalene to their respective fractions with crystallized phytosterols at high purity.

SUMMARY OF THE INVENTION

[0011] The invention relates to an Integrated process for the recovery of valuable palm oil phytonutrients more particularly vitamin E, phytosterols and squalene which comprises the steps of acid/alkaline catalysed esterification/transesterification process of palm oil with lower alkyl alcohol, multi-stage vacuum distillation of alkyl esters, saponification of the phytonutrients concentrate, crystallization of phytosterols and finally partitioning of vitamin E and squalene with organic solvents.

[0012] Crude palm oil was estertfied in alkyl alcohol preferably methanol and ethanol using sodium hydroxide or potassium hydroxide as catalyst to substitute the glycerol portion of glycerides with alkyl groups for the production of alkyl esters and glycerol. The type of alkyl alcohols used depending on the volatility of the alkyl esters produced in which the lower boiling point alkyl esters with shorter alkyl chain length are preferable in this case.

[0013] The lower boiling alkyl esters were subjected to multi-stage vacuum distillation, preferably three stage short path distillation (SPD) at different operating conditions as described below. The first short path distillation served the purpose to distil about 90% of the bulk esters with minimal amount of vitamin E, phytosterols and squalene being distilled

over to the distillate. The applied short path distillation conditions are temperature ranging from 70°C to 120°C and pressure ranging from 1·33 Pa to 6·67 Pa (10m Torr to 50mTorr). The phytonutrients enriched residue was then subjected to second short path distillation in the removal of all the impurities and colouring materials/pigments including carotenes, phospholipids, glycolipids, waxes, oxidized products and other long chain hydrocarbons. The operating conditions are temperature ranging from 130°C to 200°C and pressure less than 0·133 Pa (1mTom). The distillate from the second short path distillation was subsequently subjected to the third short path distillation to produce vitamin E, phytosterols, squalene and monoglycerides concentrates in a mixture with operating temperature less than 120°C and pressure less than 0·133 Pa (1mTom).The purified concentrate is free from all indigenous heavy molecules which is critical in the following separation and purification processes.

[0014] To the purifed concentrate, saponification process was carried out in the presence of hydroxide and alcohol. They hydroxides used are sodium hydroxide and potassium hydroxide whereas alcohols used including methanol, ethanol and iso-propanol. Preferably, the saponification process is carried out using potassium hydroxide or sodium hydroxide at 10% concentration and refluxed in alcohol for 30 minutes to one hour under inert gas blanketing, wherein the inert gas is preferably nitrogen. The unsaponifiable materials were recovered using hydrocarbon solvents extraction of the reaction mixture such as heptane, hexane, iso-octane and petroleum ether. The hydrocarbon layer was neutralized with copious of water washing and the unsaponifiable matters recovered containing only vitamin E, phytosterols and squalene.

[0015] Phytosterols were crystallized out from the unsaponifiable mixture using water/alcohol/hydrocarbon system by heating and cooling processes preferably from 65°C - 85°C to 10°C-30°C. The crystallized phytosterols were filtered and to the remaining-part of the mixture, hydrocarbon solvent and alkyl alcohol was introduced to partitioning the less polar squalene into hydrocarbon layer and the relatively more polar vitamin E into the alkyl alcohol layer. The alkyl alcohols used including methanol, butanol and iso-propanol and hydrocarbon solvents used including hexane, heptane and iso-octane. Preferably, the unsaponifiable material is mixed with hydrocarbon solvent, short chain C_1 to C_4 alcohol and water of ratio 25:1:1 and heated to temperature of 65°C to 80°C and slowly cooled to temperature of 10°C to 30°C to crystallized phytosterols. Further preferred is a method wherein the filtrate is mixed with hydrocarbon solvent and short chain C_1 to C_4 alcohol of ratio 5:3 to partition the non-polar squalene into hydrocarbon layer and polar vitamin E into alcohol layer.

[0016] In a preferred embodiment of the invention, the process comprises the following steps :

(i) first stage short path distillation carried out on the methyl esters obtained by the conversion of crude palm oil into palm oil methyl esters at a temperature of 70°C to 120°C and pressure between 1.33 Pa to 6.67 Pa (1 0m Torr to 50mTorr);
(ii) second stage short path distillation carried out on the residue obtained in step (i) at a temperature of 130°C to 200°C and pressure less than 0.133 Pa (1mTorr);
(iii) third stage short path distillation carried out on the distillate obtained in step (ii) at a temperature below 120°C and pressure less than 0.133 Pa (1mTorr);
(iv) saponification of the residue obtained in step (iii) carried out using potassium hydroxide or sodium hydroxide at 10% concentration and refluxed in alcohol for 30 minutes to one hour under nitrogen blanketing;
(v) mixing the unsaponifiable material in step (iv) with hydrocarbon solvent, short chain C_1 to C_4 alcohol and water of ratio 25:1:1 and heating mixture to temperature of 65°C to 85°C and cooling slowly to temperature of 25°C to 30°C to crystallize phytosterols;
(vi) mixing filtrate obtained in step (v) with a hydrocarbon selected from the group consisting of heptane, hexane or iso-octane and a short chain C_1 to C_4 alcohol selected from the group consisting of methanol, ethanol, butanol or iso-propanol in ratio 5:3 to partition non-polar squalene into hydrocarbon layer and polar vitamin E into alcohol layer;
(vii) separating two layers and subsequently adding hydrocarbon selected in step (vi) into the alcohol layer and short chain C_1 to C_4 alcohol selected in step (vi) into the hydrocarbon layer to further partition the vitamin E and squalene and
(viii) extracting squalene from the hydrocarbon layer and extracting vitamin E from the alcohol layer.

DESCRIPTION OF THE DRAWING

[0017]

Figure 1 shows a schematic representation of the extraction process of the phytonutrients concentrate.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The invention will now be described with reference to Figure 1 and to the following steps as example of the steps involved in the extraction process. The quantities used and parameters used are by way of example only and are

not limited thereto unless otherwise stated.

Example 1

[0019] 5kg of crude palm oil was esterfied with 2.5 kg of methanol and 50g of NaOH as catalyst. The methyl esters were separated from glycerol and neutralized by water washing. Methyl esters were subjected to the first short path distillation at temperature of 90°C and pressure of 2·67 Pa (20mTorr). The residue was then subjected to second short path distillation under operating temperature of 150°C and pressure of 0·133Pa (1mTorr) to remove all coloured materials/ pigments. The light yellowish distillate was subsequently subjected to third short path distillation with temperature of 90°C and pressure of 2·67 Pa (1mTorr) for the production of vitamin E, phytosterols and squalene (phytonutrients) concentrates. The detailed analysis results of the phytonutrients concentrates are shown in Table 1.

Example 2

[0020] 3 grams of the purified phytonutrients concentrates as obtained from Example 1 or from other sources was saponified using 5ml of 10% KOH and 20ml of ethanol. The mixture was refluxed under nitrogen blanketing for 30 minutes. The reacted mixture was transferred into a separating funnel with 10ml of ethanol, 20ml of hot distilled water and 30ml of hexane. The mixture was shaken and cooled to room temperature leaving hexane layer at the top and aqueous layer at the bottom. The unsaponifiable materials, which is hexane soluble was collected from the top whereas the aqueous layer was further extracted 5 times with 30ml hexane/Water of ratio 9:1. The hexane layer recovered was neutralized with water washing and all the solvents was removed by rotary-evaporator and vacuum pump drying. Recovery of vitamin E, phytosterols and squalene are 83%, 93% and 86%. The detailed analysis results are shown In Table 2.

Example 3

[0021] 0.42 grams of the unsaponifiable materials from saponification of purified phytonutrients concentrates as obtained from Example 2 or from other sources was added with 5ml of ethanol, 5ml of hexane and 0.5 ml of distilled water. The mixture was shaken to a homogeneous stage and settled into two layers. The hexane layer at the top was separated from the ethanol/water layer at the bottom. Solvents were removed using rotary-evaporabor and vacuum pump dryer. The concentration of squalene in hexane layer is 41% with recovery of 97% and the concentration of sterols in ethanol layer is 64.7% with recovery of 52.9%. The concentration of vitamin E in hexane and ethanol layers is 12% and 20.4%. The detailed analysis results are shown in Table 3.

Example 4

[0022] 0.8 grams of the unsaponifiable matters with phytosterols concentration of 39.4% from saponification of purified phytonutrients concentrates as obtained from Example 3 or from other sources was added with 2.5 ml hexane, 0.1 ml methanol and 0.1 ml distilled water. The mixture was heated to 70°C and cooled slowly to 28°C. The solid crystal formed was filtered with suction and washed with copious amount of hexane. The solvents in the filtrate were rotary evaporated and vacuum pump dried. The concentration of phytosterols is 99% with recovery of 63.5%. The detailed analysis results are shown in Table 4.

Example 5

[0023] 0.73 grams of the unsaponifiable matters with phytosterols concentration of 39,4% from saponification of purified phytonutrients concentrates was added as obtained from Example 4 or from other sources with 3.5 ml hexane, 0.1 ml methanol and 0.1 ml distilled water. The mixture was heated to 70°C and cooled slowly to 28°C. The solid crystal formed was filtered with suction and washed with copious amount of hexane. The solvents in the filtrate were rotary evaporated and vacuum pump dried. The concentration of phytosterols is 99% with recovery of 41.7%. The detailed analysis results are shown in Table 5.

Example 6

[0024] 0.69 grams of the unsaponifiable matters with phytosterols concentration of 39.4% from saponification of purified phytonutrients concentrates as obtained from Example 5 or from other sources was added with 25 ml hexane, 0.05 ml methanol and 0.1 ml distilled water. The mixture was heated to 70°C and slowly cooled to 28°C. The solid crystal formed was filtered with suction and washed with copious amount of hexane. The solvents in the filtrate were rotary evaporated and vacuum pump dried. The concentration of phytosterols is 99% with recovery of 36.8%. The detailed analysis results

are shown in Table 6.

Example 7

[0025] 0.71 grams of the unsaponifiable matters with phytosterols concentration of 54.4% from saponification of purified phytonutrients concentrates as obtained from Example 6 or from other sources was added with 25 ml hexane, 0.1 ml methanol and 0.1 ml distilled water. The mixture was heated to 70°C and slowly cooled to 28°C. The solid crystal formed was filtered with suction and washed with copious amount of hexane. The solvents in the filtrate were rotary evaporated and vacuum pump dried. The concentration of phytosterols is 99% with recovery of 41%. The detailed analysis results are shown in Table 7.

Example 8

[0026] 0.29 grams of the filtrate obtained from Example 5 or other solvents after crystallisation of phytosterols was added with 5ml hexane and 2ml methanol. The mixture was shaken to a homogeneous stage and settled into two layers. The hexane layer at the top was separated from the methanol layer at the bottom. Solvents were removed using rotary-evaporator and vacuum pump dryer. The concentration of vitamin E in methanol layer is 31.3% with recovery of 52.6% and the concentration of squalene in hexane layer is 51% with recovery of 87.5%. The detailed analysis results are shown in Table 8.

Example 9

[0027] 0.34 grams of the filtrate obtained from Example 7 or other solvents after crystallisation of phytosterols was added with 5ml hexane and 3ml methanol. The mixture was shaken to a homogeneous stage and settled into two layers, The hexane layer at the top was separated from the methanol layer at the bottom. Solvents were removed using rotary-evaporator and vacuum pump dryer. The concentration of vitamin E is 51.2% with recovery of 57.5% and the concentration of squalene in hexane layer is 44.2% with recovery of 95.4%. The detailed analysis results are shown in Table 9.

Example 10

[0028] . The filtrate of the unsaponifiable matters after crystallisation of phytosterols from purified phytonutrients concentrate was treated with serial partitioning of organic solvents to enhance the concentration of vitamin E and squalene. 0.6g of filtrate was added with 5ml of hexane and 3ml of methanol. The mixture was chilled to 15°C for 15 minutes. The hexane layer was separated from methanol layer and analysed, 1ml of hexane was subsequently added to methanol layer and 1ml of methanol was added to hexane layer. After chilling to 15°C for another 15 minutes, all the hexane and methanol layers were separated. All samples were analysed for vitamin E and squalene contents. The concentration of vitamin E in methanol phase after second partitioning of methanol layer is 79.3% with recovery of 34.9%. The concentration of squalene in hexane phase after second partitioning of hexane layer is 77.2% with recovery of 65.5%. The detailed analysis results are shown in Table 10. The process is described in Figure 2.

Table 1

Sample Code	Percentage (%)									
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	Undetermined Products
Crude Palm Oil Methyl Esters	0.00	98.13	1.11	0.22	0.06	0.07	0.06	0.05	0.06	ND
Residue (1st Stage SPD)	0.00	84.09	9.99	2.87	0.78	0.84	0.67	0.47	0.64	ND
Residue (2nd Stage SPD)	0.00	2.40	0.00	43.57	7.82	0.00	1.11	0.71	4.99	39.40
Residue (3rd Stage SPD)	0.00	5.78	53.69	3.94	0.53	6.56	8.40	3.98	0.12	ND
Distillate (1st Stage SPD)	0.00	99.00	0.05	0.00	0.00	0.00	0.00	0.01	0.00	ND
Distillate (2nd Stage SPD)	0.00	89.40	8.96	0.07	0.00	0.59	0.62	0.41	0.02	ND
Distillate (3rd Stage SPD)	0.00	98.33	0.25	0.00	0.00	0.00	0.00	0.01	0.00	ND

Table 2

Sample Code	Percentage (%)									Weight (g)
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	
Purified Phytonutrients Conc	0	4.48	68.33	0	1.04	8.39	15.06	6.66	0.05	3.03
Unsaponifiable Materials	3.8	0.0	0.0	0.0	2.5	20.5	52.4	20.7	0.2	0.81

Table 3

Sample Code	Percentage (%)									
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	Weight (g)
Unsaponifiable Materials (Starting materials)	3.6	0.0	0.0	0.0	2.9	25.5	49.5	18.2	0.1	0.42
Hexane Layer	2.3	0.0	0.0	0.0	4.9	41.0	39.7	12.0	0.1	0.26
EtOH Layer	5.3	0.0	0.0	0.0	0.3	9.3	64.7	20.4	0.1	0.17

Table 4

Sample Code	Percentage (%)									
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	Weight (g)
Unsaponifiable Materials (Starting materials)	8.8	0.0	0.0	0.3	3.2	33.7	39.4	14.1	0.3	0.79
Filtrate	11.3	0.0	0.0	0.5	3.9	46.9	18.4	17.2	0.5	0.61
Solid	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.19

Table 5

Sample Code	Percentage (%)									Weight (g)
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	
Unsaponifiable Materials (Starting materials)	8.8	0.0	0.0	0.3	3.2	33.7	39.4	14.1	0.3	0.73
Filtrate	10.7	0.0	0.0	0.6	4.2	43.2	24.6	16.2	0.4	0.61
Solid	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.12

Table 6

Sample Code	Percentage (%)									
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	Weight (g)
Unsaponifiable Materials (Starting materials)	8.8	0.0	0.0	0.3	3.2	33.7	39.4	14.1	0.3	0.69
Filtrate	10.0	0.0	0.0	0.4	3.5	41.0	28.9	15.7	0.3	0.59
Solid	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.10

Table 7

Sample Code	Percentage (%)									
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	Weight (g)
Unsaponifiable Materials (Starting materials)	1.8	0.0	0.0	0.0	2.5	18.5	54.4	22.7	0.2	0.71
Crystallized Phytosterols	0.0	0.0	0.0	0.0	0.0	0.0	99.0	0.0	0.0	0.16
Filtrate	3.0	0.0	0.0	0.0	4.8	30.0	35.9	26.2	0.2	0.55

Table 8

Sample Code	Percentage (%)									
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	Weight (g)
Filtrate (Starting materials)	11.7	0.0	0.0	0.0	3.7	42.2	21.4	16.4	0.5	0.29
Hexane Layer	11.3	0.0	0.0	0.4	4.6	51.0	17.4	10.3	0.5	0.21
MeOH Layer	10.2	0.0	0.0	0.0	1.7	23.6	33.0	31.3	0.3	0.08

Table 9

Sample Code	Percentage (%)									
	FFA	Esters	MG	DG	TG	Squalene	Sterols	Vitamin E	Carotenes	Weight (g)
Filtrate (Starting materials)	3.0	0.0	0.0	0.0	4.8	30.0	35.9	26.2	0.2	0.34
Hexane Layer	1.2	0.0	0.0	0.0	9.3	44.2	27.1	17.1	0.2	0.22
MeOH Layer	4.3	0.0	0.0	0.0	0.8	5.4	38.1	51.2	0.1	0.10

Table 10

Sample Code	Percentage (%)									Weight (g)
	FFA	Esters	MG	DG	TG	Sterols	Squalene	Vitamin E	Carotenes	
Filtrate	8.56	0.00	0.00	0.00	0.00	18.20	36.55	36.70	0.30	0.60
Hexane 1	3.12	0.00	0.00	0.00	0.00	8.78	69.10	19.00	0.20	0.25
Hexane 2	4.00	0.00	0.00	0.00	0.00	11.72	54.12	30.16	0.30	0.12
Hexane 3	1.57	0.00	0.00	0.00	0.00	8.70	77.21	12.52	0.30	0.19
Methanol 1	9.92	0.00	0.00	0.00	0.00	15.10	18.18	56.80	0.20	0.31
Methanol 2	1.69	0.00	0.00	0.00	0.00	13.85	5.12	79.33	0.20	0.10
Methanol 3	0.01	0.00	0.00	0.00	0.00	22.10	18.37	59.52	0.10	0.04

Claims

1. A method of extraction of phytosterols, squalene and vitamin E from crude palm oil comprising the steps of:-

   a) conversion of crude palm oil into palm oil methyl esters;

b) three stage short path distillation of crude palm oil methyl esters obtained in 1 (a) to yield phytonutrients;
c) saponification of phytonutrients concentrate from 1(b);
d) crystallisation of phytosterols, and
e) solvents partitioning of vitamin E and squalene.

2. A method of extracting phytosterols, squalene and Vitamin E as claimed in Claim 1, wherein a first short path distillation is carried out at temperature of 70°C to 120°C and pressure between 1.33 Pa to 6.67 Pa (10m Torr to 50m Torr).

3. A method of extracting phytosterols, squalene and Vitamin E as claimed in Claim 2, wherein a second short path distillation is carried out at temperature of claim 130°C to 200°C and pressure less than 0.133 Pa (1mTorr).

4. A method of extracting phytosterols, squalene and Vitamin E as claimed in Claim 3 wherein a third short path distillation is carried out at temperature below 120°C and pressure less than 0.133 Pa (1mTorr).

5. A method as claimed in any one of Claims 1 to 4, wherein the saponification process of phytonutrients concentrate is carried out using potassium hydroxide or sodium hydroxide at 10% concentration and refluxed in alcohol for 30 minutes to one hour under inert gas blanketing.

6. A method as claimed in Claim 5, wherein the inert gas is nitrogen.

7. A method as claimed in Claim 5 or Claim 6, wherein unsaponifiable material is mixed with hydrocarbon solvent, short chain C_1 to C_4 alcohol and water of different ratios.

8. A method as claimed in Claim 7, wherein the unsaponifiable material is mixed with hydrocarbon solvent, short chain C_1 to C_4 alcohol and water of ratio 25:1:1 and heated to temperature of 65°C to 85°C and slowly cooled to temperature of 10°C to 30°C to crystallize phytosterols.

9. A method as claimed in Claim 8 wherein the filtrate is mixed with hydrocarbon solvent and short chain C_1 to C_4 alcohol of ratio 5:3 to partition the non-polar squalene into hydrocarbon layer and polar vitamin E into alcohol layer.

10. A method as claimed in any one of Claims 7 to 9, wherein the hydrocarbon solvents including heptane, hexane and iso-octane and short chain C_1 to C_4 alcohols including methanol, ethanol, butanol and iso-propanol.

11. A method according to claim 1 comprising the steps of:-

(i) first stage short path distillation carried out on the methyl esters obtained in step 1(a) at a temperature of 70°C to 120°C and pressure between 1.33 Pa to 6.67 Pa (1 OmTorr to 50mTorr);
(ii) second stage short path distillation carried out on the residue obtained in step (i) at a temperature of 130°C to 200°C and pressure less than 0.133 Pa (1mTorr);
(iii) third stage short path distillation carried out on the distillate obtained in step (ii) at a temperature below 120°C and pressure less than 0.133 Pa (1mTorr);
(iv) saponification of the residue obtained in step (iii) carried out using potassium hydroxide or sodium hydroxide at 10% concentration and refluxed in alcohol for 30 minutes to one hour under nitrogen blanketing;
(v) mixing the unsaponifiable material in step (iv) with hydrocarbon solvent, short chain C_1 to C_4 alcohol and water of ratio 25:1:1 and heating mixture to temperature of 65°C to 85°C and cooling slowly to temperature of 25°C to 30°C to crystallize phytosterols;
(vi) mixing filtrate obtained in step (v) with a hydrocarbon selected from the group consisting of heptane, hexane or iso-octane and a short chain C_1 to C_4 alcohol selected from the group consisting of methanol, ethanol, butanol or iso-propanol in ratio 5:3 to partition non-polar squalene into hydrocarbon layer and polar vitamin E into alcohol layer;
(vii) separating two layers and subsequently adding hydrocarbon selected in step (vi) into the alcohol layer and short chain C_1 to C_4 alcohol selected in step (vi) into the hydrocarbon layer to further partition the vitamin E and squalene, and
(viii) extracting squalene from the hydrocarbon layer and extracting vitamin E from the alcohol layer.

Patentansprüche

1. Verfahren zum Extrahieren von Phytosterolen, Squalen und Vitamin E aus Rohpalmöl, folgende Schritte umfassend:

   a) Überführen von Rohpalmöl in Palmölmethylester;
   b) Dreistufen-Kurzwegdestillation von Rohpalmölmethylestern, die in 1(a) erhalten wurden, um Phytonährstoffe zu erhalten;
   c) Verseifung des Phytonährstoffkonzentrats aus 1(b);
   d) Kristallisation von Phytosterolen; und
   e) Lösungsmitteltrennung von Vitamin E und Squalen.

2. Verfahren zum Extrahieren von Phytosterolen, Squalen und Vitamin E nach Anspruch 1, worin eine erste Kurzwegdestillation bei einer Temperatur von 70 °C bis 120 °C und einem Druck von 1,33 Pa bis 6,67 Pa (10 mTorr bis 50 mTorr) durchgeführt wird.

3. Verfahren zum Extrahieren von Phytosterolen, Squalen und Vitamin E nach Anspruch 2, worin eine zweite Kurzwegdestillation bei einer Temperatur von 130 °C bis 200 °C und einem Druck von weniger als 0,133 Pa (1 mTorr) durchgeführt wird.

4. Verfahren zum Extrahieren von Phytosterolen, Squalen und Vitamin E nach Anspruch 3, worin eine dritte Kurzwegdestillation bei einer Temperatur unter 120 °C und einem Druck von weniger als 0,133 Pa (1 mTorr) durchgeführt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, worin der Verseifungsvorgang eines Phytonährstoffkonzentrats unter Verwendung von Kaliumhydroxid oder Natriumhydroxid in einer Konzentration von 10 % und Rückfluss in Alkohol über einen Zeitraum von 30 Minuten bis zu einer Stunde unter einer Inertgasdecke durchgeführt wird.

6. Verfahren nach Anspruch 5, worin das Inertgas Stickstoff ist.

7. Verfahren nach Anspruch 5 oder Anspruch 6, worin nicht verseifbares Material mit Kohlenwasserstofflösungsmittel, kurzkettigem C_1- bis C_4-Alkohol und Wasser in unterschiedlichen Verhältnissen vermischt wird.

8. Verfahren nach Anspruch 7, worin nicht verseifbares Material mit Kohlenwasserstofflösungsmittel, kurzkettigem C_1- bis C_4-Alkohol und Wasser in einem Verhältnis von 25:1:1 vermischt und auf eine Temperatur von 65 °C bis 85 °C erhitzt und langsam auf eine Temperatur von 10 °C bis 30 °C abgekühlt wird, um Phytosterole zu kristallisieren.

9. Verfahren nach Anspruch 8, worin das Filtrat mit Kohlenwasserstofflösungsmittel und kurzkettigem C_1- bis C_4-Alkohol und Wasser in einem Verhältnis von 5:3 vermischt wird, um das nichtpolare Squalen in die Kohlenwasserstoffphase und polares Vitamin E in die Alkoholphase zu trennen.

10. Verfahren nach einem der Ansprüche 7 bis 9, worin die Kohlenwasserstofflösungsmittel Heptan, Hexan und Isooctan und die C_1- bis C_4-Alkohole Methanol, Ethanol, Butanol und Isopropanol umfassen.

11. Verfahren nach Anspruch 1, folgende Schritte umfassend:

    (i) eine erste Kurzwegdestillationsstufe, die an den in Schritt 1(a) erhaltenen Methylestern durchgeführt wird, bei einer Temperatur von 70 °C bis 120 °C und einem Druck von 1,33 Pa bis 6,67 Pa (10 mTorr bis 50 mTorr);
    (ii) eine zweite Kurzwegdestillationsstufe, die an dem in Schritt (i) erhaltenen Rückstand durchgeführt wird, bei einer Temperatur von 130 °C bis 200 °C und einem Druck von weniger als 0,133 Pa (1 mTorr);
    (iii) eine dritte Kurzwegdestillationsstufe, die an dem in Schritt (ii) erhaltenen Destillat durchgeführt wird, bei einer Temperatur unter 120 °C und einem Druck von weniger als 0,133 Pa (1 mTorr);
    (iv) Verseifung des in Schritt (iii) erhaltenen Rückstands, durchgeführt unter Verwendung von Kaliumhydroxid oder Natriumhydroxid in einer Konzentration von 10 % und Rückfluss in Alkohol über einen Zeitraum von 30 Minuten bis zu einer Stunde unter einer Stickstoffdecke;
    (v) Mischen des nicht verseifbaren Materials aus Schritt (iv) mit Kohlenwasserstofflösungsmittel, kurzkettigem C_1- bis C_4-Alkohol und Wasser in einem Verhältnis von 25:1:1 und Erhitzen des Gemischs auf eine Temperatur von 65 °C bis 85 °C und langsames Abkühlen auf eine Temperatur von 25 °C bis 30 °C, um Phytosterole zu kristallisieren.
    (vi) Mischen des in Schritt (v) erhaltenen Filtrats mit einem Kohlenwasserstoff, ausgewählt aus der aus Heptan,

Hexan und Isooctan bestehenden Gruppe, und einem kurzkettigen C_1- bis C_4-Alkohol, ausgewählt aus der aus Methanol, Ethanol, Butanol und Isopropanol bestehenden Gruppe, in einem Verhältnis von 5:3, um unpolares Squalen in die Kohlenwasserstoffphase und polares Vitamin E in die Alkoholphase zu trennen;
(vii) Trennen der beiden Phasen und darauf folgendes Zusetzen von in Schritt (vi) ausgewähltem Kohlenwasserstoff zur Alkoholphase und in Schritt (vi) ausgewähltem C_1- bis C_4-Alkohol zur Kohlenwasserstoffphase, um das Vitamin E und das Squalen weiter zu trennen;
(viii) Extrahieren von Squalen aus der Kohlenwasserstoffphase und Extrahieren von Vitamin E aus der Alkoholphase.

Revendications

1. Un procédé d'extraction de phytostérols, de squalène et de vitamine E à partir d'huile de palme brute, comprenant les étapes de :

   a) conversion d'huile de palme brute en esters méthyliques d'huile de palme ;
   b) distillation à court trajet à trois étages des esters méthylique d'huile de palme obtenus dans 1 (a) pour donner des phytonutrients ;
   c) saponification du concentré de phytonutrients de 1(b) ;
   d) cristallisation de phytostérols ; et
   e) compartimentage par solvants de la vitamine E et du squalène.

2. Un procédé d'extraction de phytostérols, de squalène et de vitamine E tel que revendiqué à la Revendication 1, dans lequel une première distillation à court trajet est mise en oeuvre à une température de 70°C à 120°C et à une pression entre 1,33 Pa et 6,67 Pa (10 mTorr à 50 mTorr).

3. Un procédé d'extraction de phytostérols, de squalène et de vitamine E tel que revendiqué à la Revendication 2, dans lequel une seconde distillation à court trajet est mise en oeuvre à une température de 130°C à 200°C et à une pression inférieure à 0,133 Pa (1 mTorr) .

4. Un procédé d'extraction de phytostérols, de squalène et de vitamine E tel que revendiqué à la Revendication 3, dans lequel une troisième distillation à court trajet est mise en oeuvre à une température en dessous de 120°C et à une pression inférieure à 0,133 Pa (1 mTorr) .

5. Un procédé tel que revendiqué dans l'une quelconque des Revendications 1 à 4, dans lequel le processus de saponification de concentré de phytonutrients est mis en oeuvre en utilisant de l'hydroxyde de potassium ou de l'hydroxyde de sodium à une concentration de 10% et une mise au reflux dans de l'alcool pendant 30 minutes à une heure sous une couverture de gaz inerte.

6. Un procédé tel que revendiqué à la Revendication 5, dans lequel le gaz inerte est l'azote.

7. Un procédé tel que revendiqué à la Revendication 5 ou à la Revendication 6, dans lequel la matière non-saponifiable est mélangée avec un solvant hydrocarboné, un alcool en C_1 à C_4 à chaîne courte et de l'eau en différents rapports.

8. Un procédé tel que revendiqué à la Revendication 7, dans lequel la matière non-saponifiable est mélangée avec un solvant hydrocarboné, un alcool en C_1 à C_4 à chaîne courte et de l'eau dans un rapport de 25:1:1 et chauffée à une température de 65°C à 85°C, puis lentement refroidie à une température de 10°C à 30°C pour cristalliser les phytostérols.

9. Un procédé tel que revendiqué à la Revendication 8, dans lequel le filtrat est mélangé avec un solvant hydrocarboné et un alcool en C_1 à C_4 à chaîne courte dans un rapport de 5:3 pour compartimenter le squalène non polaire en couche hydrocarbonée et la vitamine E polaire en couche alcoolique.

10. Un procédé tel que revendiqué dans l'une quelconque des Revendications 7 à 9, dans lequel les solvants hydrocarbonés comprennent l'heptane, l'hexane et l'iso-octane, et les alcools en C_1 à C_4 à chaîne courte comprennent le méthanol, l'éthanol, le butanol et l'isopropanol.

11. Un procédé selon la Revendication 1 comprenant les étapes de:

(i) distillation à court trajet de premier étage mise en oeuvre sur les esters méthyliques obtenus dans l'étape 1 (a) à une température de 70°C à 120°C et à une pression entre 1,33 Pa et 6,67 Pa (10 mTorr à 50 mTorr) ;
(ii) distillation à court trajet de second étage mise en oeuvre sur le résidu obtenu dans l'étape (i) à une température de 130°C à 200°C et à une pression inférieure à 0,133 Pa (1 mTorr) ;
(iii) distillation à court trajet de troisième étage mise en oeuvre sur le distillat obtenu dans l'étape (ii) à une température en dessous de 120°C et à une pression inférieure à 0,133 Pa (1 mTorr) ;
(iv) saponification du résidu obtenu dans l'étape (iii) mise en oeuvre en utilisant de l'hydroxyde de potassium ou de l'hydroxyde de sodium à une concentration de 10% et une mise au reflux dans l'alcool pendant 30 minutes à une heure sous une couverture d'azote ;
(v) mélanger la matière non saponifiable de l'étape (iv) avec un solvant hydrocarboné, un alcool en C_1 à C_4 à chaîne courte et de l'eau dans un rapport de 25:1:1 et chauffer le mélange à une température de 65°C à 85°C puis refroidir lentement à une température de 25°C à 30°C pour cristalliser les phytostérols ;
(vi) mélanger le filtrat obtenu dans l'étape (v) avec un hydrocarbure sélectionné dans le groupe se composant de l'heptane, de l'hexane et de l'iso-octane et un alcool en C_1 à C_4 à chaîne courte sélectionné dans le groupe se composant du méthanol, de l'éthanol, du butanol ou de l'iso-propanol dans un rapport de 5:3 pour compartimenter le squalène non polaire en couche hydrocarbonée et la vitamine E polaire en couche alcoolique;
(vii) séparer deux couches et ajouter ensuite l'hydrocarbure sélectionné dans l'étape (vi) dans la couche alcoolique et l'alcool en C_1 à C_4 à chaîne courte sélectionné dans l'étape (vi) dans la couche hydrocarbonée pour compartimenter en outre la vitamine E et le squalène ; et
(viii) extraire le squalène de la couche hydrocarboné et extraire la vitamine E de la couche alcoolique.

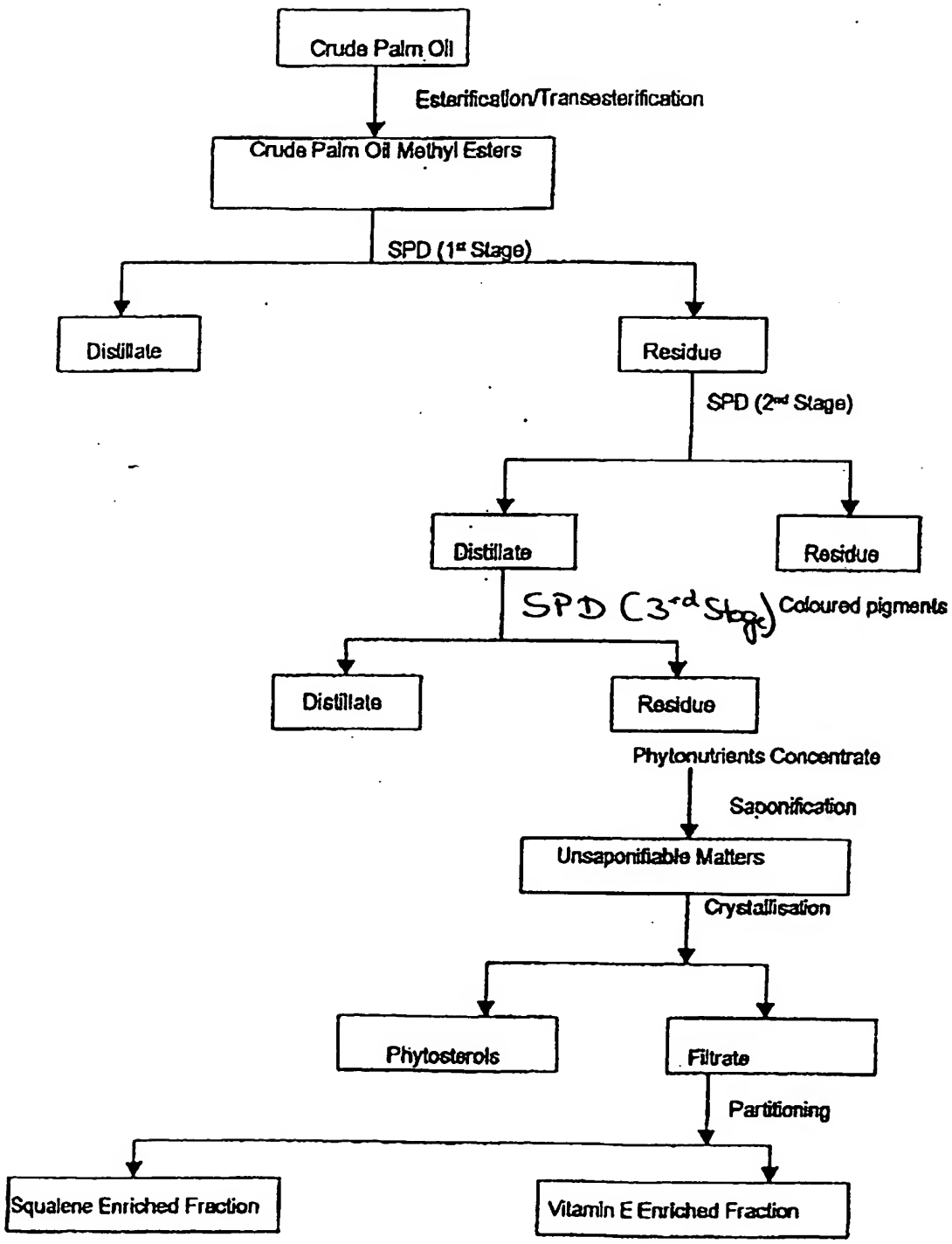
Crude Palm Oil
Esterification/Transesterification
Crude Palm Oil Methyl Esters
SPD (1st Stage)
Distillate
Residue
SPD (2nd Stage)
Distillate
Residue
SPD (3rd Stage)
Coloured pigments
Distillate
Residue
Phytonutrients Concentrate
Saponification
Unsaponifiable Matters
Crystallisation
Phytosterols
Filtrate
Partitioning
Squalene Enriched Fraction
Vitamin E Enriched Fraction

FIGURE 1